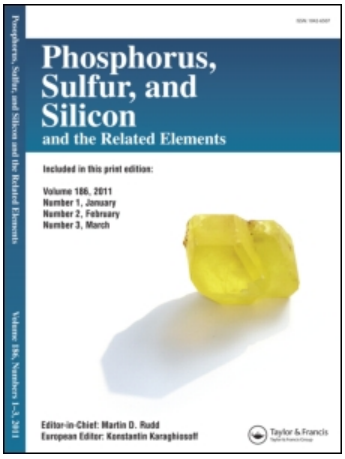

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MOLYBDENUM-SULPHUR BOND-STRENGTH BOND-LENGTH RELATIONSHIPS

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MOLYBDENUM-SULPHUR BOND-STRENGTH BOND-LENGTH RELATIONSHIPS

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Empirical parameters (d_1 and N) are given for the equation $s = (d/d_1)^{-N}$ relating the molybdenum-sulphur bond length (d, Å) and its bond strength (s, valence units) for the cation in the formal oxidation states from +3 to +6, using structural data from 61 compounds with 82 different (S), (O,S), (N,S) and (O,N,S) ligand sets. Parameter values (d_1,N) are: 2.320, 6.6; 2.224, 5.6 or 2.251, 4.6; 2.201, 5.0 and 2.167, 5.8 for sulphur bonding to Mo(VI), Mo(V), Mo(IV) and Mo(III), respectively.

INTRODUCTION

Molybdenum sulphides, thiomolybdates and chelate complexes with sulphur ligands are of interest for general considerations of metal-sulphur bonding and electron delocalization. Whereas the metal complexes are being studied mainly in relation to their biological activity,[1] many of the other compounds find wide and diverse applications in industry and chemical technology, as lubricants, pigments and semiconducting and thermoelectric materials.[2] To this is to be added that molybdenum compounds are also practically used as catalysts for various chemical processes, as ammoxidation, disproportionation, naphtha reforming, etc. Catalytic activity is brought about by the molybdenum atom having incomplete inner shells. As a result of the ease of transfer from one valency state to another, molybdenum may function either as a donor or as an acceptor of electrons.

The significant attention that molybdenum chemistry has received has prompted a number of molecular structural investigations using X-ray diffraction techniques. In turn, the results of these studies provide impetus for further considerations. The character of the chemical bond, structure, valence state and distribution of electron density in the bonds are main directions for theoretical investigation, requiring detailed knowledge of the molecular structure. The abundance of literature dealing with molybdenum-sulphur complexes also calls for a systematic examination of their structures with a view towards establishing empirical bond-strength (s) bond-length (d) relations of the Mo—S bonds, especially in relation to the existence of molybdenum-ligand π-bonding. This paper, therefore, will focus on deriving such relationships for molybdenum complexes containing sulphur ligands. It is noticed that previously defined parameter sets for the $s = f(d)$ expressions of cation-sulphur bonds are limited to Fe.[3] On the other hand, molybdenum-anion bonding has recently been examined extensively for oxygen and nitrogen.[4,5]

RESULTS AND DISCUSSION

Analytical bond-strength bond-length relations are usually expressed in the non-linear form $s = (d/d_1)^{-N}$, where d_1 and N are empirical values subject to Pauling's[6] constraint that the cation

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valence is calculated by summation of s over all the bonds formed by the cation. From an examination of all-oxygen molybdenum coordination spheres it appears in a first approximation that the expression $s = (d/1.882)^{-6.0}$ is applicable to all Mo—O bonds, independently of the valence state of the cation.[4] The relations $s = (d/1.950)^{-5.75}$ and $s = (d/1.893)^{-5.1}$ have been reported for Mo(VI)—N and Mo(V)—N bonds, respectively.[5]

Structural data concerning the *regular* molybdenum-sulphur coordination spheres of Table I lead to the following reference values from which bond-strength bond-length curves may be obtained: (compound, Mo oxidation state, bond length (Å), bond strength (v.u.)); $MoS_4(C_4N_2H_{12})$, $(NH_4)_2MoS_4$ and $CuNH_4MoS_4$, VI, 2.183(6), 1.5; $Mo(S_2C_2H_2)_3$, VI, 2.33(2), 1.0 (however, *vide infra*);

$[Mo(S_2CNEt_2)_4]_2(Mo_6O_{19})$

and $Mo(S_2CNEt_2)_4Cl$, V, 2.516 (5), 0.625; $(Ph_4As)_2[Mo(mnt)_3]$, IV, 2.374 (4), 0.667; $Mo(S_2CNEt_2)_4$, $Mo(S_2CMe)_4$ and $Mo(S_2CPh)_4$, IV, 2.518 (3), 0.50. Additional reference points are derived from Table 2 after allowance for the oxygen contribution to the total valence sum: Cs_2MoOS_3, VI, 2.178 (5), 1.54; $Mo_2O_4(S_2CNEt_2)_2$, V, 2.455 (1), 0.675; $MoO(S_2CNPr^n_2)$, IV, 2.413 (2), 0.48; $Mo_2(S_2COEt)_4 \cdot 2C_4H_8O$, II, 2.478 (1), 0.48. Comparison of structural data for $Mo_2O_4 \cdot (\text{L-histidine})_2 \cdot 3H_2O$ (Table I of Ref. 5) with

$Mo_2S_2O_2 \cdot (\text{L-histidine})_2 \cdot 1\frac{1}{2}H_2O$

(Table IV), of

$Na_2Mo_2O_4[SCH_2CH(NH_2)CO_2]_2 \cdot 5H_2O$

with

$Na_2Mo_2S_2O_2[SCH_2CH(NH_2)CO_2]_2 \cdot 2H_2O$

and of $Mo_2O_4[SCH_2CH(NH_2)COOEt]_2$ with $Mo_2S_2O_2[SCH_2CH(NH_2)COOMe]_2$ suggests that Mo(V)—S = 2.322 Å corresponds to Mo(V)—O = 1.928 Å (or 0.87 v.u.) The initially obtained parameter sets based on these data were refined by minimizing the discrepancies of the calculated valence sum and formal oxidation states using all available structural results (Tables I–IV). The Mo(III)—S parameters were derived by variation of the Mo(IV) data. The following Mo—S bond-strength bond-length equations $s = (d/d_1)^{-N}$ were then found: (d_1, N, Mo valence state); 2.320, 6.6, VI; 2.251, 4.6 or 2.224, 5.6, V; 2.201, 5.0, IV and 2.167, 5.8, III. Mo(II)—S parameters were not defined due to lack of sufficient reference data. Scarcity of reliable all-sulphur Mo(V) coordinations leads to a high

TABLE I

Bond-strengths and bond-lengths in molybdenum-sulphur coordination spheres

Compound[a]	Bond distances(Å) Mo-S	Mo-Mo	Formal Mo valence state	Σs_{Mo-S}[b,c]	σ_d[d]	Structural unit	Reference
$MoS_4(C_4N_2H_{12})$	2.168, 2.171, 2.197, 2.199	-	6.0	5.97(4)	0.007	MoS_4[e]	a
$(NH_4)_2MoS_4$	2.171, 2.177(2x), 2.186	-	6.0	6.07(3)	0.005	MoS_4[e]	n
$CuNH_4MoS_4$	2.19(4x)	-	6.0	5.85(15)	0.03	MoS_4[e]	o
$(\eta\text{-}C_5H_4CH_3)_2Mo_2S_4$	2.141(2x), 2.247(2x)	2.970(1)	6.0	6.04(1)	0.001	MoS_4[e]	p
$Mo(S_2C_6H_4)_3$	2.360(2x), 2.370(2x), 2.371(2x)	-	6.0	5.26(1)	0.002	MoS_6[f]	q
$Mo(S_2C_2H_2)_3$	2.33(6x)	-	6.0	5.83(6)	0.02	MoS_6[f]	r
syn-$Mo_2S_4(S_2CNBu^n_2)_2$	1.935, 2.304, 2.309, 2.445, 2.448 1.939, 2.304, 2.310, 2.442, 2.452	2.801(2) 2.801(2)	5.0 5.0	5.16(1) 5.13(1)	0.004 0.004	(MoS_5[g] (	s
$[Mo(S_2CNEt_2)_4]_2(Mo_6O_{19})$	2.518, 2.525, 2.526, 2.530(2x), 2.544, 2.548, 2.549	-	5.0	4.64(1)	0.005	MoS_8[h]	t
$Mo(S_2CNEt_2)_4Cl$	2.479, 2.489, 2.492, 2.494, 2.497, 2.504, 2.511, 2.516	-	5.0	4.96(1)	0.005	MoS_8[h]	t
syn-$[Mo_2S_4(S_2C_2H_4)_2](NEt_4)_2$	2.089, 2.313, 2.322, 2.403, 2.407 2.112, 2.320, 2.323, 2.406, 2.407	2.863(2) 2.863(2)	5.0 5.0	4.13(2) 4.04(2)	0.003 0.003	(MoS_5[g] (	u
anti-$[Mo_2S_4(S_2C_2H_4)_2](NEt_4)_2$	2.129, 2.298, 2.344, 2.387, 2.414	2.878(2)	5.0	4.01(2)	0.003	MoS_5[g]	u
$(Ph_4As)_2[Mo(mnt)_3]$	2.367(2x), 2.371(2x), 2.383(2x)	-	4.0	4.11(2)	0.004	MoS_6[i]	v
MoS_2 (rhombohedral)	2.387(6x)	n.d.	4.0	4.00(-)	n.d.	MoS_6[f]	w

MoS_2(hexagonal)	2.41(6x)	n.d.	4.0	3.81(15)	0.06	MoS_6[f]	x
Bu_4N.[Mo(mnt)$_2$(dtc)]	2.353,2.355,2.358,2.362,2.454,2.456	-	4.0	4.00(1)	0.004	MoS_6[f]	y
$Mo(S_2CMe)_4$	2.499(2x),2.501(2x),2.530(2x),2.534(2x)	-	4.0	4.10(2)	0.002	MoS_8[h]	z
$Mo(S_2CPh)_4$	2.475(4x),2.543(4x)	-	4.0	4.17(4)	0.001	MoS_8[h]	aa
$Mo(S_2CNEt_2)_4$	2.520(2x),2.524(2x),2.535(2x),2.537(2x)	-	4.0	4.00(2)	0.003	MoS_8[i]	bb
$CoMo_2S_4$	2.344,2.366,2.384,2.411,2.544,2.582 2.364,2.432,2.466,2.497,2.511,2.582 2.307,2.352,2.435,2.450,2.533,2.577 2.366,2.387,2.407,2.508,2.528,2.618	2.756-3.564(7)[k]	3.0	3.10(4) 2.82(4) 3.09(4) 2.89(4)	0.010 0.010 0.010 0.010	(MoS_6[l]	cc
$CoMo_2S_4$	2.375,2.391(2x),2.502(2x),2.568	n.d.	3.0	2.96(-)	n.d.	MoS_6[l]	dd
$Ga_xMo_2S_4$	2.42(3x),2.59(3x)	2.84(-)	3.0	2.65(-)	n.d.	MoS_6[l]	ee
$[Mo(S_2O)(S_2CNEt_2)_2]_2$	2.368,2.391,2.468,2.479,2.485,2.506,2.549 2.363,2.403,2.475,2.476,2.490,2.515,2.535	2.757(1) 2.757(1)	3.0 3.0	3.36(1) 3.35(1)	0.003 0.003	(MoS_7	ff
$Mo_{2.06}S_3$	2.34,2.39(2x),2.54(2x),2.72 2.31-2.40(2x),2.51(2x),2.55	2.85-3.22(2) 2.87-3.22(2)	2.91 2.91	2.84(12) 3.04(15)	0.04 0.04	(MoS_6[l]	gg
$Al_xMo_2S_4$	2.37(3x),2.58(3x)	2.89(-)	2.88	2.88(-)	n.d.	MoS_6[l]	ee
Mo_3S_4	2.425,2.426,2.431,2.439,2.460	2.698-3.084(-)	2.67	2.54(-)	n.d.	MoS_5[g]	hh
$Pb_{0.92}Mo_6S_{7.5}$	2.393,2.456,2.460,2.512,2.566	2.572-2.737(3)	2.19	2.32(3)	0.009	MoS_5[g]	ii
$NiMo_3S_4$	2.408,2.451,2.460,2.477,2.496	2.691-2.765(-)	2.0	-	n.d.	MoS_5[g]	jj

[a] Bu^n, *n*-butyl; dtc, *N*,*N*-diethyldithiocarbamate; Et, ethyl; Me, methyl; mnt, maleonitriledithiol; Ph, phenyl.

[b] Calculated with the following parameter sets (d_1 and N of $s = (d/d_1)^{-N}$): 2.320, 6.6 (VI); 2.251, 4.6 (V); 2.201, 5.0 (IV); 2.167, 5.8 (III).

[c] In valence units. Standard deviations were estimated for the shortest *d*-value of the set.

[d] In Ångstrom units.

[e] Tetrahedron.

[f] Trigonal prism.

[g] Square pyramid.

[h] Dodecahedron.

[i] D_3 symmetry. Trigonal compression is midway between values for octahedron and trigonal prism.

[j] Square antiprism.

[k] Mo_4 clusters.

[l] Octahedron.

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TABLE II

Bond strengths and bond-lengths in molybdenum-oxygen and -sulphur coordination spheres

Compound[a]	Bond distances(Å) Mo-O	Mo-S	Mo-Mo	Formal Mo valence state	Σs[b,c]	σ[d]	Structural unit	Reference
$MoO(S_2)(S_2CNPr^n_2)_2$	1.667	2.354,2.390,2.450,2.509,2.522,2.663	-	6.0	6.07(10)	0.013	MoS_6O[e]	k
$Cs_2[MoO(S_2)_2(COSCO_2)]$	1.70,2.31	2.38(4x), 2.53	-	6.0	6.07(28)	0.04	MoS_5O_2[e]	l
$MoO_2(S_2CNEt_2)_2$	1.634(2x)	2.443(2x),2.629(2x)	-	6.0	6.97(18)	0.025	MoS_4O_2[f]	m
$MoO_2(S_2CNPr^n_2)_2$	1.695,1.696	2.446,2.457,2.621,2.681	-	6.0	5.96(3)	0.005	MoS_4O_2[f]	n
Cs_2MoOS_3	1.785	2.176,2.179(2x)	-	6.0	5.92(5)	0.010	$MoSO_3$[g]	o
$Mo_2O_3[S_2P(OEt)_2]_4 \cdot 2C_6H_4Cl_2$	1.647,1.863	2.442,2.497,2.547,2.801	-	5.0	5.15-5.06(11)	0.013	MoS_4O_2[f]	p
$Mo_2O_3(S_2COEt)_4$	1.644,1.851 1.649,1.872	2.458,2.509,2.530,2.690 2.469,2.508,2.540,2.715	- -	5.0 5.0	5.27-5.17(28) 5.11-5.05(28)	0.033 0.033	(MoS_4O_2[f] (	q
$Mo_2O_3(S_2CSPr^i)_4$	1.687,1.844	2.468,2.510,2.565,2.694	-	5.0	4.92-4.92(9)	0.013	MoS_4O_2[f]	r
$Mo_2O_3(S_2CNPr^n_2)_4$	1.666,1.870 1.676,1.856	2.440,2.491,2.515,2.669 2.440,2.491,2.536,2.687	- -	5.0 5.0	5.11-5.07(10) 5.04-5.03(10)	0.013 0.013	(MoS_4O_2[f] (	n
$[MoO[S_2P(iso\text{-}C_8H_7O)_2]_2]_2O$	1.639,1.862	2.457,2.515,2.528,2.832	-	5.0	5.18-5.07(13)	0.015	MoS_4O_2[f]	s
$Mo_2O_3(SPh)_2(S_2CNEt_2)_2$	1.683,2.006 1.683,2.015	2.452,2.487,2.501,2.702 2.441,2.465,2.505,2.673	2.683(2) 2.683(2)	5.0 5.0	4.61-4.68(6) 4.64-4.73(6)	0.009 0.009	(MoS_4O_2[f] (	t
syn-$[Mo_2O_2S_2[S_2C_2(CN)_2]](Bu^n_4N)_2$	1.661 1.666	2.292,2.300,2.433,2.444 2.294,2.299,2.425,2.435	2.821(2) 2.821(2)	5.0 5.0	4.99-4.97(6) 4.97-4.96(6)	0.007 0.007	(MoS_4O[h] (	u
$Mo_2O_3S(S_2CNPr^n_2)_2$	1.665,1.927	2.305;[2.45(2x)][i]	2.673(3)	5.0	[4.93]-[5.20](8)	0.011	MoS_3O_2[h]	v
$Mo_2O_4(S_2CNEt_2)_2$	1.677,1.940(2x) 1.680,1.940,1.943	2.447,2.457 2.456,2.459	2.580(1) 2.580(1)	5.0 5.0	4.82-4.64(2) 4.78-4.61(2)	0.002 0.002	(MoS_2O_3[h] (	w
$MoO(S_2CNPr^n_2)_2$	1.664	2.410,2.412,2.413,2.418	-	4.0	4.61(6)	0.008	MoS_4O	n
$Mo_2(S_2COEt)_4 \cdot 2C_4H_8O$	2.795	2.475,2.477,2.479,2.480	2.125(1)	2.0	n.d.	0.001	Mo_2S_8[i]	x

[a] Bu^n, *n*-butyl; Et, ethyl; Pr^i, isopropyl; Pr^n, *n*-propyl.

[b] Calculated with the following parameter sets (d_1, N) of the equation $s = (d/d_1)^{-N}$: Mo—O (1.882, 6.0); Mo(VI)—S (2.320, 6.6); Mo(IV)—S (2.201, 5.0). For Mo(V) coordinations the following sets were used: Mo(V)—O (1.882, 6.0), Mo(V)—S (2.224, 5.6) and Mo(V)—O (1.859, 5.0), Mo(V)—S (2.251, 4.6), respectively.

[c] In valence units. Standard deviations were estimated for the shortest *d*-value of the set.

[d] E.s.d. of d_{Mo-O} in Ångstrom units.

[e] Pentagonal bipyramid.

[f] Octahedron.

[g] Tetrahedron.

[h] Square pyramid.

[i] The Mo_2^{4+} binuclear unit is coordinated at eight sites. These may be considered to be at the corners of eclipsed squares whose centers are occupied by the metal ions.

[j] Data assumed by comparison with $Mo_2S_4(S_2CNBu^n_2)_2$ (Ref. 20).

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TABLE III

Bond-strengths and bond-lengths in molybdenum-nitrogen and -sulphur coordination spheres

Compound[a]	Bond distances (Å) Mo-N	Mo-S	Mo-Mo	Suggested Mo valence states	r_s[b,c]	σ_d[d]	Structural unit	Reference
$MoN(S_2CNEt_2)_3$	1.618	2.503,2.511,2.515,2.536,2.541,2.851	-	6.0	6.07(10)	0.014	MoS_6N^e	h
$[\{MoN(S_2CNEt_2)_3\}_2.$	1.632	2.484,2.487,2.491,2.507,2.509,2.647	-	not given	6.29(-)	n.d.	MoS_6N^g	h
$Mo(S_2CNEt_2)_3](PF_6)_3$	1.646	2.487,2.495,2.496,2.498,2.504,2.740	-	not given	6.07(-)	n.d.	MoS_6N^g	
	2.140,2.147	2.490,2.501,2.517,2.526,2.531,2.532	-	not given	3.07+[1.00][m]	n.d.	$MoS_6N_2^f$	
$Mo(N_2EtPh)(S_2CN(CH_2)_5)_3BPh_4$	1.715	2.48,2.50(3x),2.51,2.55	-	6.0	5.32(10)	0.016	MoS_6N^g	i
$Mo(S_2CNBu^n_2)_3(NO)$	1.731	2.463,2.507,2.513,2.528,2.529,2.568	-	4.0,3.0,2.0	5.17(4)	0.008	MoS_6N^e	i
$Mo(S_2CNMe_2)_3(NS)$	1.743	2.491,2.496,2.502,2.525,2.544,2.604	-	4.0,3.0	5.06(5)	0.01	MoS_6N^e	h
$Mo(N_2CO_2Et)(dtc)_3$	1.732	<2.508> (5x),2.604	-	4.0	5.13(2)	0.005	MoS_6N^e	k
$Mo(NHC_6H_4S)_2(S_2CNEt_2)$	2.001,2.009	2.376,2.392,2.473(2x)	-	5.0	2.46+[1.50][m]	0.002	$MoS_4N_2^g$	l

[a] Bu", *n*-butyl; dtc, *N*,*N*-dimethyldithiocarbamate; Et, ethyl; Me, methyl; Ph, phenyl.

[b] Calculated according to the following (d_1, N) parameter sets of the expression $s = (d/d_1)^{-N}$: Mo(VI)—N, 1.950, 5.75; Mo(V)—N, 1.893, 5.1; Mo(VI)—S, 2.320, 6.6; Mo(V)—S, 2.251, 4.6; Mo(IV)—S, 2.201, 5.0.

[c] In valence units. Standard deviations were estimated for the shortest *d*-value of the set.

[d] E.s.d. of d_{Mo-N} in Ångstrom units.

[e] Pentagonal bipyramid.

[f] Dodecahedron.

[g] Octahedron with trigonal prismatic distortion.

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[m] Estimated s_{Mo-N} contribution.

interdependency of the Mo—S *s*-*d* relation on the values used for Mo(V)—O. In fact, it turns out that a combination of (d_1, N) sets for Mo(V)—O and Mo(V)—S of (1.882, 6.0) and (2.224, 5.6) is equivalent to the use of (1.859, 5.0) and (2.251, 4.6) respectively (*cf.* Table II). Once more confidence is gained in Mo—S bond-strength bond-length relationships, following up new data concerning regular all-sulphur coordination spheres, the mixed (O, S) molybdenum coordinations can eventually be used to revise the Mo—O parameter sets for the reduced cation. Indeed, such corrections are expected. For example, on the basis of the (1.882, 6.0) parameter set for Mo(VI)—O the calculated valence sums for Mo(II)—O bonds always slightly exceed the nominal value of 2.0 v.u. by about 0.12 v.u. if account is taken of the contribution of the more distant anions coaxial with the Mo—Mo bond. (Table 1 of Ref. 4). It has been argued by Pyatenko[7] that such anions which are not significantly screened by the closest anions are to be included in the coordination sphere of the cation as otherwise a considerable part of the valence forces of the cation is omitted. This is in accordance with our experience that secondary bonding effects need to be considered to properly account for the valence balance of s^2-type cations.[8]

A detailed examination of the results shows that the proposed parameter sets essentially well account for the formal oxidation states in a great variety of structures with different ligand sets, stereogeometries, valence states, coordination numbers, and including quadruply, triply, doubly or singly bridged oxo, nitrido or sulphido dimeric structures, complexes with terminal, bridging and complex atoms or with one to three terminal atoms (usually oxygen), either in the presence or absence of cation-cation interaction (metal-metal bonding). The average deviation from the ideal valence values in Table I is 3.7%, usually better than 2.6%, although there are individual deviations up to about 12% in some structures. Similar

TABLE IV

Bond-strengths and bond-lengths in Mo(O, N, S) coordination spheres

Compound[a]	Bond distances (Å) Mo-O	Mo-N	Mo-S	Mo-Mo	Formal Mo valence state	Σs[b,c]	σ_d[d]	Structural unit	Reference
$Mo_2O_3(oxine)_2(SCH_2CH_2O)$	1.693,1.943,2.021,2.201 1.693,1.930,2.039,2.178	2.201 2.209	2.484 2.484	2.628(1) 2.628(1)	5.0 5.0	4.76(4) 4.78(4)	0.005 0.005	(MoO_4SN[e] (	h
$Na_2Mo_2O_4\{SCH_2CH(NH_2)CO_2\}_2.5H_2O$	1.706,1.915,1.946,2.295 1.712,1.907,1.954,2.295	2.260 2.200	2.490 2.491	2.569(2) 2.569(2)	5.0 5.0	4.77(10) 4.78(10)	0.015 0.015	(MoO_4SN[e] (	i
$Cs_2(Mo_2S_2O_2.EDTA).2H_2O$	1.683,2.102,2.120	2.448	2.289,2.298	2.799(1)	5.0	4.91(4)	0.006	MoO_3S_2N[e]	j
$Mo_2O_4\{SCH_2CH(NH_2)COOEt\}_2$	1.669,1.919,1.924 1.657,1.930,1.957	2.241 2.197	2.393 2.378	2.562(3) 2.562(3)	5.0 5.0	4.90(15) 4.96(15)	0.018 0.018	(MoO_3SN[f] (	k
syn-$Na_2Mo_2S_2O_2\{SCH_2CH(NH_2)CO_2\}_2.2H_2O$	1.69,2.38 1.55,2.35	2.31 2.22	2.30,2.34,2.51 2.32,2.37,2.48	2.820(3) 2.820(3)	5.0 5.0	4.60(18) 5.94(35)	0.025 0.025	(MoO_2S_3N[e] (	l
$\{Mo_2S_2O_2(L\text{-histidine})_2\}.1\frac{1}{2}H_2O$	1.686,2.213 1.666,2.204	2.245,2.257 2.237,2.272	2.314,2.323 2.331,2.342	2.848(1) 2.848(1)	5.0 5.0	4.72(5) 4.81(5)	0.006 0.006	($MoO_2S_2N_2$[e] (	m
$Mo_2O_3(C_5H_4NS)_4$	1.673,1.853	2.185,2.305	2.433,2.483	-	5.0	5.11(3)	0.004	$MoO_2S_2N_2$[e]	n
$Mo_2O(PhCON_2)_2(S_2CNEt_2)_2.CH_2Cl_2$	2.04,2.06 1.66	1.90,1.92 1.96,1.97	<2.450>(2x) <2.450>(2x)	2.662(-) 2.662(-)	5.0 5.0	4.27(2) 4.93(5)	0.006 0.006	$MoO_2S_2N_2$[f] $MoOS_2N_2$[g]	o
$Mo_2O(ClC_6H_4CSN_2)_2(S_2CNEt_2)_2.CHCl_3$	1.67	<1.97>(2x)	<2.437>(2x)	n.d.	5.0	4.88(8)	0.01	$MoOS_2N_2$[g]	p
$MoO(Me_2N_2)(S_2CNMe_2)_2$	1.71	1.85	2.43,2.52,2.58,2.72	-	5.0	5.22(7)	0.01	$MoOS_4N$[e]	q
syn-$Mo_2S_2O_2\{SCH_2CH(NH_2)COOMe\}_2$	1.650 1.779	2.23 2.24	2.296,2.304,2.369 2.302,2.325,2.387	2.804(4) 2.804(4)	5.0 5.0	4.99(25) 4.10(15)	0.03 0.03	$MoOS_3N$[f]	r

[a] EDTA, ethylenediaminetetraacetate; Et, ethyl; Me, methyl; oxine, 8-hydroxyquinoline; Ph, phenyl.
[b] Calculated according to the following (d_1, N) parameter of the expression $s = (d/d_1)^{-N}$: Mo—O (1.882,6.0), Mo—N (1.893, 5.1), Mo—S (2.224, 5.6).
[c] In valence units. Standard deviations were estimated for the shortest d-value of the set.
[d] E.s.d. of d_{Mo-O} on Ångstrom units.
[e] Octahedron.
[f] Trigonal bipyramid.
[g] Square pyramid.
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figures for Tables II, III and IV are (4.0, 2.7, 15%), (2.6, 2.1, 6%), and (5.7, 3.4, 18%), respectively. Part of the discrepancies is due to uncertainties in the bond-length values, as indicated by the errors given for the bond-strength sums. Account should be taken of the fact that although many interatomic distances are quoted with standard errors of 0.005 Å or less, systematic errors are usually larger; therefore, the true standard errors are higher than the values quoted. This obviously would improve the agreement between the bond-strength sums and the valence. It has been proposed[9] that second-nearest neighbours might account for some of the additional deviations.

It is of interest to examine evidence for genuine effects in the observed discrepancies. The main departures from ideal values in Table I concern $[Mo(S_2O)(S_2CNEt_2)_2]_2$, $Ga_xMo_2S_4$ and especially $Mo(S_2C_6H_4)_3$ and the $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ anions. The mean Mo—S distance in $Mo(S_2C_6H_4)_3$ (2.367(6) Å) has been recognized by Cowie and Bennett[10] as being long and more similar to bond lengths in $[MoS_6C_6(CN)_6^{2-}]$.[11] *Tris*(dithiolene) and related structures are known for their oxidation state problem.[12,13] In these structures the formal charge on the metal appears to de-

pend strongly upon the electron withdrawing ability of the ligand (*cf.* $Mo(S_2C_6H_4)_3$ and $Mo(S_2C_2H_2)_3$). The poor calculated datum for $Mo(S_2C_6H_4)_3$ is thus eventually rationalised. Similar oxomolybdenum complexes have been discussed elsewhere.[4] Reported bond data for the Mo(V) complexes $[Mo_2S_4(S_2C_2H_4)_2](NEt_4)_2$ and $Mo_2S_4(S_2CNBu^n_2)_2$ suggest a considerable difference in total bond valence (about 1 v.u.), mainly due to the (terminal) Mo—S_t bond lengths. Consequently, this appears to cast doubt on the proposed oxidation state of the metal in the 1,2-dimercaptoethanatomolybdate anion although other (unspecified) factors cannot be quite excluded.[14]

As to the results of Table II, it is noticed that the parameter values defined in this paper establish the (VI)-valent state for the cation in the product $Mo(S_2C_2H_2)_3$, VI, 2.33(2), 1.0 (however, *vide infra*); from reaction of $MoO_2(S_2CNPr_2)_2$ and H_2S. Similarly, the problem of the oxidation state of another compound containing S_2 groups as ligands, namely $Cs_2[MoO(S_2)_2(COSCO_2)]$, is settled.[16] Poor fits in Tables II and IV relate to

$MoO_2(S_2CNEt_2)_2$, $MoO(S_2CNPr^n_2)_2$,

$Mo_2O(PhCON_2)_2(S_2CNEt_2)_2 \cdot CH_2Cl_2$,

$Na_2Mo_2S_2O_2[SCH_2CH(NH_2)CO_2]_2 \cdot 2H_2O$

and $Mo_2S_2O_2[SCH_2CH(NH_2)COOMe]_2$. As to $MoO_2(S_2CNEt_2)_2$, the present calculation, the anomaly in its *cis*-MoO_2 structure[17] and the quite normal behaviour of the Pr^n-analogue (Table 2) allow to discard this complex. Structural data for the latter two compounds reveal pronounced and unexplained dissimilarities between apparently equivalent cations. As the deviations are in opposite directions no common effect can be invoked. It appears that the Mo—O lengths of about 1.65 Å would be more genuine values for these structures. The other discrepancies and the overall low calculated bond valence sums of Table IV, which generally fall short by about 3.4%, may be partly on account of the use of the bond-strength bond-length relationships beyond the experimentally verified ranges.

Published information on the oxidation state of many molybdenum complexes is extremely contradictory. Several examples have already been given above; others concern the thio-oxine (quinoline-8-thiol) complexes[18] and further cases are amongst the (N, S) ligand sets (Table III). Clearly, the latter contain several well-defined structural types, such as pentagonal bipyramidal coordinations with average bond lengths of Mo—N 1.632 Å, Mo—S 2.504 (5x)–2.75 Å and Mo—N 1.730 Å, Mo—S 2.506 (5x)–2.58 Å and dodecahedral environments with Mo—N 2.143 Å (2x), Mo—S 2.516 Å (6x). In all cases the *trans* effect of the Mo—N bond length on the axial Mo—S bond is quite pronounced. Calculated bond valence sums for the pentagonal bipyramidal structures indicate oxidation states of VI and V, whereas the dodecahedron is best in accordance with the IV valent state of the cation. The same holds for the octahedral structure $Mo(NHC_6H_4S)_2(S_2CNEt_2)$. In fact, although no parameter set has been derived for Mo(IV)–N bonds, it is quite reasonable to attribute bond valences of about 0.5 and 0.75 v.u. to such Mo—N bond lengths of about 2.14 and 2.00 Å (*cf.* Table III). It should be mentioned here that although molybdenum is fairly unequivocally in the VI oxidation state in $MoN(S_2CNEt_2)_3$, electrochemical and XPS measurements appear to be more consistent with Mo(IV).[19]

From a survey of Tables I–IV it appears that a terminal sulphur atom is observed only in $Mo_2S_4(S_2CNBu^n_2)_2$,[20] where the Mo(V)—S bond length of 1.937(4) Å corresponds to about 2.1 v.u. The Mo(VI)—S bonds in the tetrahedral complexes $MoS_4(C_4N_2H_{12})$,[21] $(NH_4)_2MoS_4$,[22] $CuNH_4MoS_4$[23] and Cs_2MoOS_3[24] with an experimentally observed average bond length of 2.183(6) Å (1.5 v.u.) are to be compared with 1.764 Å in molybdates.[8] It is noticed that the coordination chemistry of Mo(VI) is almost entirely that of oxo-complexes and that nonoxo-complexes, such as MoS_4^{2-}, are rare. In analogy to the case of oxomolybdenum (VI) configurations no undistorted octahedral sulphur coordination sphere around Mo(VI) has been found, if we disregard the *tris* (dithiolene) and related structures, such as $Mo(S_2C_2H_2)_3$[25] and $Mo(S_2C_6H_4)_3$[26] for reasons mentioned above.

The chemistry of Mo(V), like that of Mo(VI), is dominated by the presence of strong Mo—O bonding, leading to either one or two short Mo—O_t distances. The oxo anion thus shows more pronounced π-donor qualities than sulphur ligands. However, unlike the Mo(VI)-state, where monomeric and polymeric complexes are dominant, dimeric species play a major role in the Mo(V) state. The dinuclear compounds in Tables I, II, and IV are bridged either by an oxo and sulphido

ligand[27] or, more usually by two sulphido ligands; triply bridged structures also occur, *e.g.* $Mo_2O_3(SCH_2CH_2O)(oxine)_2$[28] and

$(pyH)_3 \cdot [Mo_2O_4(MeCO_2)(NCS)_4]$.[29]

Although most of the dimeric compounds contain a single terminal Mo—O_t linkage on each Mo, in case of $Mo_2S_4[(n\text{-}C_4H_9)_2dtc]_2$[20] and $[Mo_2S_4(S_2C_2H_4)_2](NEt_4)_2$[14] $Mo_2S_4^{2+}$-groupings have been observed, which are similar to the usual $Mo_2O_4^{2+}$-structure with sulphur replacing both the bridging *and terminal* oxygens. As there is considerable biological interest in $Mo_2(\mu\text{–}S)_2$ complexes it is worthwhile to consider the main bond valence parameters of this framework. The average Mo(V)—Mo(V) distance is 2.816 Å, indicating a single metal-metal bond and the Mo(V)—S bond length of 2.312 Å corresponds to about 0.85 v.u. This value differs considerably from the estimate of Drew *et al.*[30] who consider the Mo—S bond order in $Mo_2(\mu\text{—}S)_2$ to be 1.5, assuming Mo(V)—S single and double bonds of 2.5 and 2.1 Å, respectively. Comparable bond-strength values of 0.84 and 0.89 v.u. were found in case of $(\mu\text{—}O)_2$ and $(\mu\text{—}N)_2$-bridged dimeric molybdenum complexes, respectively.[5] The Mo(V)—O and Mo(V)—S bond lengths of 1.927(11) and 2.305(5) Å in a Mo(μ—O)(μ—S)Mo bridge[27] are in line with these results. At variance to oxo-complexes no linear Mo—S—Mo bridges have been observed. Compounds reported to contain formal Mo(V)—S single bonds are:

$Mo_2O_2(cysteine)_2(\mu\text{—}S)_2$,[30]

$Mo_2O_2(cysteine)_2(\mu\text{—}O)_2$,[31]

$Na_2Mo_2O_2(cysteine)_2(\mu\text{—}O)_2 \cdot 5H_2O$[32]

and

$Mo_2O_2(S_2COEt)_4(\mu\text{—}O)$[33]

with bond lengths of 2.37–2.51 Å. The present analysis attributes bond strengths of 0.75–0.55 v.u. to such Mo—S bonds.

Complexes of Mo(IV) are mostly monomeric structures with regular coordination polyhedra. The average octahedral and dodecahedral bond lengths amount to 2.390 and 2.518 Å, corresponding to 0.66 and 0.51 v.u. (calculated values). As may be seen from Tables I–IV, the Mo(III) structural chemistry is scantily studied and mostly consists of sulphide structures, partly of intervalent nature. The molybdenum (II)-sulphur crystal chemistry is as poorly developed and consists of a cluster compound[34] and a dimeric Mo_2^{4+} complex characterized by Mo—Mo bonding.

All calculations were performed on the Oxford University ICL 1906A computer.

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